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"MAGNETIC HARDENING STUDIES AND NOVEL TECHNIQUES FOR PREPARATION OF HIGH PERFORMANCE MAGNETS"

FINAL REPORT

GEORGE C. HADJIPANAYIS

DECEMBER 18, 1998

U. S. ARMY RESEARCH OFFICE

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UNIVERSITY OF DELAWARE

I. STATEMENT

This study was focused on the search, fabrication and characterization of novel hard magnetic materials with large magnetization and anisotropy and high Curie temperature, which can be used for the development of less expensive and stronger permanent magnets.

II. SUMMARY OF RESULTS

Our studies were focused on the interstitial nitrides and carbides and on nanocomposite magnets. In the case of carbides, the materials were made from the melt and this is very promising for the future production of anisotropic magnets by sintering. This is not true for nitrides where nitrogenated materials decomposed upon heating to temperatures above 500° C. We had successfully used both melt-spinning and mechanical alloying to obtain large coercivities in the 2:17 and 1:12 compounds.

Our work in the preparation of nanocomposite magnets was focused on the Fe-rich Nd-Fe-B system with a microstructure consisting of a fine mixture of hard (2:14:1) and soft (Fe) phases which showed enhanced values of reduced remanences, $M_R/M_S >$ 0.5, with relatively high coercivity. This effect allows the production of more economical magnets since additional processing is not required for enhanced remanence and the amount of rare earth used is significantly lower.

NITRIDES AND CARBIDES

Nitrogenated $Nd(FeM)_{12}$ (M = Mo, Ti, and V) Compounds

$Nd(FeM)_{12}$ (M = Mo, Ti, and V) compounds with an ultrafine grain microstructure were obtained by mechanical alloying after milling for 50 hours in a SPEX 8000 Mixer/Mill. The high-energy ball milling leads to a nanocrystalline structure which is a mixture of α-Fe with some amorphous phase. The ultrafine grain size was found to be about 500 Å by x-ray diffraction and electron microscopy. A $ThMn_{12}$ type compound was formed after heat-treating at 800° C for 30 minutes. After nitrogenation, at around 650° C with the gas phase interstitial modification process, the $Nd(FeM)_{12}$ structure had been observed to be stable and with increased lattice parameters. Our experimental data showed that the increase in unit cell volume, $\Delta V/V$, is larger in mechanically alloyed powders than in as-cast alloy powders. The change of the unit cell volume, $\Delta V/V$ for M - Ti, Mo, and V is 5.5, 3.0, and 3.6, respectively.

The interstitial nitrogen atoms lead to an increase of saturation magnetization M_s, the Curie temperature T_c, and anisotropy K with values $\Delta M_s/M_s$ = 16-43%, and $\Delta T_c/T_c$ = 30—32%. The nitrogen content was found to be very sensitive to the coercivity. A maximum N content of x = 10% in the $Nd_{10}Fe_{75}Mo_{15}N_x$ sample was obtained after nitrogenation at 650° C for 2 hours resulting in the best hard magnetic properties, H_c = 8.0 kOe, M_s = 64.5 emu/g and T_c = 310° C. The value of N content is much higher in the mechanically alloyed powders than in as-cast alloys.

A small amount of Dy was used to improve the hard magnetic properties. An increase in coercivity by 2-3 kOe was obtained by the addition of 1.5 at % Dy in the $Nd_{8.5}Dy_{1.5}Fe_{75}No_{15}N_x$ compound. Al-bonded magnets were also made with mechanically alloyed powders using Al in the range of 5-40 wt% and bonding temperatures in the range of 600 - 680° C. An average increase of the coercivity by about $\Delta H_c = 2.0$ kOe was observed. The highest coercivity obtained in bonded magnets was 9.5 kOe when the bonding temperature was close to the melting temperature of Al (at 660° C for 1 hour).

Ga and Al Substituted $Sm_2(Fe, Ga, Al)_{17}$ Carbides Made by Arc Melting

Small Ga and Al substitutions were found to allow the incorporation of a larger amount of C in the 2:17 lattice via arc-melting. We have studied the coercivity and microstructure of melt spun $Sm_2Fe_{17-x}Ga_xC_y$ (x = 2, 3 and y = 1, 1.5, 2, 2.5) carbides as a function of composition and annealing temperature. The highest coercivity was obtained $Sm_2Fe_{14}Ga_3C_x$ (x = 2, 2.5) samples when annealed at 800 ° C for 20 minutes, with a value of 12.8 kOe at room temperature. Microstructure studies showed the coexistence of α-Fe and 2:17 carbide phases in all the samples studied. Smooth hysteresis curves characteristic of "exchange-coupled" magnets have been obtained only in samples with uniformly distributed phases having a fine grain size around 25 nm.

We have also prepared $Sm_2Fe_{14}Al_3C_x$ carbides with x ranging from 1 to 3 by arc-melting the constituent elements with a Fe-C alloy. Upon homogenization at 1110°C for 17 hours, all compounds were found to crystallize into a single Th_2Zn_{17} type phase (except $Sm_2Fe_{14}Al_3C_3$ which contains an extra small amount of α-Fe) with a unit cell volume expansion $\Delta V/V$ up to 2.1% compared with the parent compound. X-ray diffraction patterns on aligned powders showed that all the carbides have an easy c-axis anisotropy. The saturation magnetization of all compounds is around 100 emu/g while the Curie temperature T_c changes from 483 K for x = 0 to 563 K for x = 3. The room temperature anisotropy field H_A changes from 15 kOe for x = 0 to 100 kOe for x = 3. Magnetic hysteresis studies on melt spun ribbons showed that a maximum coercivity of 8 kOe can be obtained for $Sm_2Fe_{14}Al_3C_{1.5}$ when annealed at 825°C for 20 minutes. Microstructure studies are underway to determine the origin of the high coercivity.

$Sm_2Fe_{14-x}Co_xSi_2(C,N)_y$

We performed a detailed study of the structural and magnetic properties of the $Sm_2/fe_{14-x}Co_xSi_2N_y$ nitrides and carbides. The $Sm_2Fe_{14-x}Co_xSi_2N_y$ nitrides maintain the Th_2Zn_{17} type structure but with a unit cell expansion $\Delta V/V$ up to 5% compared to the host materials. On the other hand, the $Sm_2Fe_{14-x}Co_xSi_2C_z$ carbides have the Th_2Zn_{17} type structure for z = 1 and transform into the $BaCd_{11}$ type structure for z = 2. Introduction of nitrogen leads to an increase in Curie temperature from 514 to 602 K for x = 0 and from 698 to 742 K for x = 4. A similar behavior was also observed in the $Sm_2Fe_{14}Si_2C$ and $Sm_2Fe_{10}Co_4Si_2C$ carbides with a T_c of 593 and 731 K, respectively. Co substitutions with $x \geq 4$ lead to uniaxial anisotropy. The introduction of nitrogen and carbon also changes the anisotropy in $Sm_2Fe_{14}Si_2$ from planar to uniaxial. A very large anisotropy field with

H_x value of 227 kOe for $Sm_2Fe_{14}Si_2N_{2.6}$ and 276 kOe for $Sm_2Fe_{10}Co_4Si_2N_{2.3}$ is observed at low temperature (1.5 K).

$Sm_3(Fe_{0.933}Ti_{0.067})_{29}$ and its Nitride

We have also prepared the $Sm_3(Fe, Ti)_{29}$ compound and its nitride and investigated their structural and magnetic properties with emphasis on the magnetocrystalline anisotropy. Both of these compounds crystallize in the $Nd_3(Fe, Ti)_{29}$ monoclinic structure. They are ferromagnetic with a Curie temperature of 486 and 750 K, respectively, and a saturation magnetization of 157 emu/g at 4.2 K. $Sm_3(Fe_{0.933}Ti_{0.067})_{29}N_5$ compounds exhibit uniaxial anisotropy from 4.2 K to the ordering temperature. The anisotropy field is 12 T at room temperature and 25 T at 4.2 K.

NANOCOMPOSITE α-Fe/Nd-Fe-B MAGNETS

Melt-Spun

We studied the crystallization, crystal structure, microstructure, and magnetic properties of $R_6(Fe\text{-}Nb)_{88}B_6$ with R = Nd,Pr,Dy,Tb and $Nd_{3.5}(Fe\text{-}Nb)_{93}B_{3.5}$ melt-spun ribbons consisting of a fine mixture of exchange coupled magnetically hard ($R_2Fe_{14}B_1$) and soft (α-Fe) phases. The as-spun ribbons of R-rich composition crystallize in two steps: at first the $Y_3Fe_{62}B_{14}$ type + α-Fe phases are formed when R = Nd, Pr, and Dy and subsequently they transform to 2:14:1 and α-Fe upon heating above 700°C. The intermediate phase in the case of $Tb_6(Fe\text{-}Nb)_{88}B_6$ is of the $TbCu_7$ type. Very high remanences up to 145emu/g with reduced remanences ranging from 0.6 to 0.7 were also observed. The coercivity of the samples was found to vary with the R element and the hard phase content. The highest room temperature coercivity of 4.5 kOe was obtained in a $Nd_4Tb_2(Fe\text{-}Nb)_{88}B_6$ sample. The observed reversible demagnetization curves were characteristic of exchange-spring magnets.

Mechanically Alloyed

Nd-Fe-B mechanically alloyed powders were made consisting of a mixture of 2:14:1 and α-Fe magnetic phases. The Nd-Fe-B alloy powders had a mixture of an amorphous Nd-Fe-B structure and α-Fe with a fine grain size about 140 Å after ball milling for 48 hours and formed the 2:14:1 phase after a heat-treatment in the temperature range of 600 - 900° C. A strong exchange coupling between the hard and soft phase was observed for annealing at temperatures below 700° C that led to an increase in remanence. The reduced remanence was very high ($M_R/M_s = 0.64$) when the grain size of the soft phase was about 150 - 200 Å and it decreased drastically with annealing temperature dropping to 0.51 at 800° C. The large drop in M_R/M_s is due to the increase of grain size of α-Fe, which (with the high temperature annealing) is much larger than the critical dimension for optimum coupling. A substitution of Nb for Fe and of Tb for Nd in the ($NdTb0_2Fe_{14}B$+FeNb (45 wt%) sample led to an increase in coercivity up to 6.0 kOe with enhanced magnetic remanence in the range of 95-105 emu/g with corresponding reduced remanence $M_R/M_s = 0.60 - 0.68$.

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